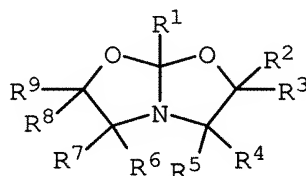


REMARKS

Claims 1-10, 12, and 13 are pending in the application. Claims 9, 10, 12, and 13 have been withdrawn from consideration as being directed to a non-elected invention. Therefore, claims 1-8 are at issue.

This response is submitted in accordance with 37 C.F.R. §1.116(a) and §1.116(b) in order to present the rejected claims in a better form for allowance or appeal. The response is necessary to eliminate rejections under 35 U.S.C. §103. This response was presented earlier, but the examiner did not fully consider or understand applicants' arguments. Therefore, applicants previous arguments are expanded upon and made more clear in this response. This response should be entered because it places the application in better form for allowance or appeal, and the amendment does not require further searching or present any new issues.

The present claims are directed to a process for postcrosslinking a water-absorbing polymer by applying a bicyclic amide acetal (I) having a structure



(I) .

In contrast to prior compounds used to postcrosslink a water-absorbing resin, the claimed bicyclic amide acetals are relatively less reactive, but still capable of reacting with carboxyl groups (specification, page 2, lines 21-23). Compound (I) also has a substantially reduced toxicity compared to other postcrosslinking compounds. In contrast to prior postcrosslinking agents, compound (I) preferably is dissolved in and applied from an inert solvent, such as alcohols, diols, and water as in Examples 2-36.

Claims 1-8 stand provisionally rejected under the judicially created doctrine of obviousness-type double patenting over claims 1, 11, and 12 of copending Application No. 10/588,671 ('671 application). Applicants traverse this rejection.

The present claims are directed to postcrosslinking of a water-absorbing polymer using a bicyclic amide acetal of formula (I). The claims of the '671 application are directed to postcrosslinking water-absorbing polymers using a surface postcrosslinker and a polyvalent cation in claimed relative amounts. The '671 application claims do not recite *any specific* surface postcrosslinker. On its face, it is submitted that the present claims and the claims of the '671 application are independent and distinct. In addition, note that the '671 application was filed *after* the present application, and the '671 application merely *disclosed* bicyclic amide acetals as a potential surface postcrosslinker because of the teachings of the present invention. The scope of the claims in the '671 patent is completely different from the present claims. It is also suggested that the examiner reconsiders the *In re Vogel* decision discussed in a previous response wherein the disclosure *may not* be used as prior art in an obviousness-type patenting rejection. Nevertheless, because this provisional double patenting rejection is not the only remaining rejection in the present application, it would be premature to address this rejection any further at this time. Applicants will consider a response to overcome this provisional obvious-type double patenting rejection in view of copending Application No. 10/588,671 should it become necessary.

Claims 1-8 stand rejected under 35 U.S.C. §103 as being obvious over Engelhardt et al. U.S. Patent No. 6,414,214 ('214) in view of Goel et al. U.S. Patent No. 4,539,376 ('376). The basis of the rejection is that, because the '214 patent discloses treating a crosslinked polymer with 2-oxazolidinone and the '376 discloses treating a maleic anhydride polymer with a bicyclic amide acetal, that it would have been obvious to post-crosslink a water-absorbent polymer with a bicyclic amide acetal. Applicants traverse this rejection.

The proper basis to establish a case of obviousness under 35 U.S.C. §103 was set forth in the Amendment "A", and is incorporated herein by reference for the sake of brevity.

The '214 patent discloses hydrogel-forming polymers prepared, for example, by polymerizing acrylic acid. Although the polymers of the '214 patent can be prepared from an anhydride ('214 patent, column 3, line 47), anhydride groups *are not* present in the final polymer. During the polymerization, the anhydride groups are hydrolyzed to carboxyl groups

(e.g., '214 patent, column 7, lines 41-42 and 58-59). See Examples of the '214 patent wherein the polymers are prepared from an *aqueous* monomer solution, which hydrolyzes the anhydride groups that may be present.

Also see '214 patent, column 3, lines 8-12 stating:

"The base polymers which are subsequently surface-postcrosslinked are crosslinked polymers having acid groups which are predominantly present in the form of their salts, generally alkali metal or ammonium salts. Such polymers swell on contact with aqueous fluids to form gels."

The '214 patent therefore clearly discloses that carboxyl groups, not anhydride groups, are present in the hydrogel-forming polymers.

The examiner states in a conclusory fashion that the '214 patent must have envisioned polymers of maleic anhydride in addition to polymers of maleic acid. The examiner has no factual basis to make such a statement, and in fact states in paragraph 11 of the Office Action that maleic anhydride *would* hydrolyze to maleic acid. All polymerizations of the '214 patent are performed in water, so the '214 actually envisions *hydrolysis* of any anhydride groups to carboxyl groups. Further, anhydride containing polymers are *not* hydrogel-forming polymers, whereas the '214 patent *title* is "Mechanically Stable Hydrogel-Forming Polymers".

It also must be pointed out that the examiner's comments at paragraph 12 of the Office Action are incorrect or based on an incomplete characterization of the reference. With respect to postcrosslinking using an organic solvent ('214 patent, column 8, lines 15-16), these are *optional* solvents used in addition to water, as a full reading of the paragraph at column 8, lines 10-16 shows ("preferably in the form of an aqueous solution", "[T]he aqueous solution may contain..."). The '214 patent does not expressly state that the anhydride groups are hydrolyzed, but elementary organic chemistry makes it understood that hydrolysis occurs under the conditions of the '214 patent. In particular, it is well known in the art that *neutralized* acid groups, and particularly neutralized carboxyl groups, are necessary to provide a water-absorbent polymer. Applicants submit concurrently with this response an excerpt from "Ullman's Encyclopedia of Industrial Chemistry," pages 81 and 82, as Exhibit A,

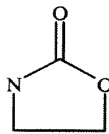
showing that the number of charges on a polymer chain is important for water absorption and swelling. (See Exhibit A, pages 81 and Figure 3).

Anhydride groups have *no* charge and cannot absorb water and swell. The '214 patent is directed to hydrogel-forming polymers (see title), so the '214 patent does *not* envision anhydride-containing polymers, as incorrectly stated by the examiner. In particular, the '214 patent teaches that charges are formed during neutralization of the crosslinked polymers ('214 patent, column 7, lines 41-52), which destroys *any* anhydride groups that may be present to form carboxylate salts. Persons skilled in the art are well aware that anhydrides easily hydrolyze in the presence of a base. See attached Exhibit B, pages 388-392 from "Advanced Organic Chemistry," Fieser et al. Reinhold Publishing Corp. (1961).

Applicants further include pages from the reference textbook "Modern Superabsorbent Polymer Technology" as Exhibit C, wherein at page 20, Chapter 2.1, it is disclosed that hydrogel-forming polymers are *only* prepared from aqueous solutions. There is *no* process known in the art using a non-aqueous solution for the production of hydrogel-forming polymers. A non-aqueous medium is necessary to retain the anhydride groups of maleic anhydride, as demonstrated by the secondary reference cited against the claims, wherein a maleic anhydride polymer is crosslinked in acetone, toluene, or in the absence of a solvent.

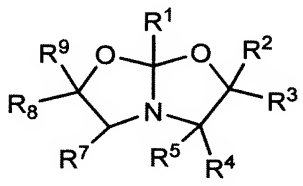
The examiner's statement that the '214 patent does not teach that polymerization must occur in aqueous solutions therefore also is incorrect. The statements that the '214 patent does not teach monomers or polymers are hydrolyzed prior to crosslinking also is incorrect, for the reasons set forth above.

In addition, as is standard in the art, the '214 patent discloses surface postcrosslinking of dried polymer particles at column 8, lines 10-51. The '214 discloses numerous compounds useful as surface crosslinkers, e.g., compounds that typically contain hydroxy (-OH), amino (-NH₂), blocked isocyanate (-NCO), and/or epoxy $\left(\text{—CH}_2\text{—}\overset{\text{O}}{\text{—}}\text{CH}_2\text{—} \right)$ groups, carbonic acid derivatives, and N-methylol compounds. One known postcrosslinker is 2-oxazolidinone disclosed at column 8, line 51 of the '214 patent and having a structure:



2-Oxazolidinone contains a carbamate moiety (-N-C(=O)-O-) that reacts with carboxyl groups of the hydrogel-forming polymer to surface crosslink the polymer particles. 2-Oxazolidinone is a monocyclic compound in no way related in structure to a claimed bicyclic amide acetal and has different functional groups.

The examiner states that a claimed amide acetal of the following structure



has a number of similarities, but few differences in structure from the 2-oxazolidinone above. Applicants submit that the differences in structure are vast, including different functional groups having different reactivities, for example the amide, ester, and carboxyl functionalities of the monocyclic 2-oxazolidinone compared to amide and ether functionalities of the bicyclic amide acetal. The only similarity is the same number of oxygen atoms and nitrogen atoms, but arranged different structurally. The examiner states that a person skilled in the art would recognize the similarities between the compounds, however, the same person would recognize the vast differences that would not lead to a substitution of one compound for the other, and the examiner has provided no facts or reasoning to support this substitution. Applicants are very comfortable pointing out these non-obvious differences in structure should this application require appeal.

The '214 patent further *specifically* discloses a preference for a surface postcrosslinker of *high* reactivity in order to achieve the benefits of the '214 patent, i.e., increased mechanical stability of polymer particles. As stated in the '214 patent at column 8, line 64 through column 9, line 13:

"The surface postcrosslinking heat treatment step provides hydrogel-forming polymers having a very low residual moisture content, typically of less than 1% by weight, frequently even of less than 0.5% by weight. It is believed that a low residual moisture content increases the brittleness of hydrogel-forming polymers, so that these products have only low mechanical stability.

According to the invention, increasing the residual moisture content to at least 3% by weight, preferably at least 4% by weight, more preferably to at least 5% by weight, increases the mechanical stability of these products considerably.

The use of surface postcrosslinkers of higher reactivity, for example ethylene glycol diglycidyl ether and its mixtures, makes it possible, through gentler temperatures, to terminate the reaction directly on obtaining a residual moisture content of at least 3% by weight."

The '214 patent therefore leads persons skilled in the art *away* from surface postcrosslinking using a compound of *lower* reactivity, such as the claimed bicyclic acetal amide.

It is well known in the art to use reactive surface postcrosslinkers in order to facilitate the surface postcrosslinking step. Reactive surface crosslinkers reduce energy requirements (i.e., require lower elevated temperatures) in the surface postcrosslinking step and maintain the esthetics of the polymer particles because surface postcrosslinking at a high temperature leads to discoloration of the polymer particle. Therefore, the art searches for and uses a surface postcrosslinker of relatively high reactivity to save energy costs and maintain polymer particle esthetics, and, in the specific case of the cited '214 patent, to provide polymer particles of high mechanical stability.

The '376 patent is directed to crosslinking maleic anhydride polymers using a bicyclic amide acetal (column 1, lines 38-41). The bicyclic amide acetal of the '376 patent is used to provide internal crosslinks between linear maleic anhydride polymers. In the '376 patent, a previously prepared maleic anhydride homopolymer or copolymer is internally crosslinked *via* the pendant anhydride moiety of the maleic anhydride using a bicyclic amide acetal. See '376 patent, column 1, lines 38-41. The '376 patent is neither directed to water-absorbing polymers nor to surface postcrosslinking. Surface postcrosslinking is substantially

different from the crosslinking disclosed in the '376 patent, and is not remotely addressed in the '376 patent.

Statements made by the examiner show a fundamental misunderstanding of hydrogel-forming polymers, and of the differences between *internal* crosslinking and *surface* postcrosslinking of a hydrogel-forming polymer. A hydrogel-forming polymer, such as an acrylic acid polymer, is an internally crosslinked polymer. Absent internal crosslinking, an acrylic acid homopolymer is water soluble and obviously cannot absorb several times its weight in water. A water-absorbing polymer is prepared either by polymerizing acrylic acid in the presence of a crosslinker or by crosslinking uncrosslinked polyacrylic acid to form crosslinks throughout the superabsorbent polymer. These crosslinks are referred to in the art as "internal crosslinks" and the crosslinker used during the polymerization is referred to in the art as an "internal crosslinking agent".

It is known that the absorbency properties of dry base polymer particles can be improved by applying a crosslinker to surfaces of the dry "base polymer" particles and forming additional crosslinks only in the vicinity of the particle surfaces, not throughout the entire volume of the particle. This process is termed "surface crosslinking" or "postcrosslinking". These two types of crosslinking, i.e., internal and surface, are separate and independent, perform different functions, are performed in separate process steps, and the two crosslinkers can be the same, but typically are different.

Surface crosslinking is therefore distinct from internal crosslinking. Also, see pages 97-103 of "Modern Superabsorbent Polymer Technology," Buchholz et al. submitted concurrently with this response in Exhibit C.

In addition, Exhibit C contains pages 6, 7, and 19-22 of the "Modern Superabsorbent Polymer Technology" reference showing that a hydrogel of the present invention necessarily is internally crosslinked. In particular, see Fig. 1.2 at page 6 providing a schematic of an internally crosslinked particle in Fig. 3.9 at page 97 of Exhibit C. Fig. 3.9 also contains a schematic of a surface crosslinked superabsorbent particle (core-shell structure) showing a higher crosslinking level on the surface shell than the internal core. Attention also is directed to Fig. 2.1 at page 20 of Exhibit C further showing the

polymerization of partially neutralized acrylic acid in the presence of a bifunctional crosslinking agent to provide an internally crosslinked superabsorbent poly(acrylate).

In the method of the '376 patent, the highly reactive anhydride group of maleic anhydride (see Exhibit B) reacts with the relatively low reacting bicyclic amide acetal. Further, the crosslinking reaction of the '376 patent is performed in an inert solvent (e.g., toluene or acetone in Examples 1-4 of the '376) or without solvent (Example 5) in order to *preserve* the highly reactive anhydride groups of the polymer for reaction with the bicyclic amide acetal. The presence of water or an alcohol would destroy the anhydride groups (see Exhibit B).

In short, the crosslinking reaction of the '376 patent between the maleic anhydride units and bicyclic amide acetal is facilitated by the high reactivity of the anhydride groups, which permits a reaction with the bicyclic amide acetal of relatively low reactivity, and wherein the inert solvent maintains the anhydride moiety so it is available for reaction.

The Court in *KSR* held that a patent composed of several elements is not proved obvious merely by demonstrating that each of the elements was, independently, known in the prior art (*KSR*, 127 S.Ct. at 1741). The court further emphasized the importance of *identifying a reason* that would have prompted a person of ordinary skill in the relevant field to combine the elements in the way the claimed new invention does, which the examiner has not provided (*Id.*, emphasis added). In this case, the examiner has provided no reasoning that would have prompted a skilled person to modify the '214 and '376 patent disclosures in a way to arrive at the present invention, i.e., to use a surface crosslinker of relatively low reactivity with relatively low reactivity carboxyl groups, when the cited references each use one reactant of relatively high reactivity.

In addition, applicants respectfully note that MPEP §§2142 and 2143 require that the teaching or suggestion to make the claimed combination and the reasonable expectation of success must both be found in the prior art, and not based on applicants' disclosure. *In re Vaeck*, 947 F.2d 4899 (Fed. Cir. 1991). The mere fact that the prior art may be modified in the manner suggested by the examiner does *not* make the modification obvious unless the prior art suggests the desirability of the modification. *In re Gordan*, 733,

F.2d at 902, 221 USPQ at 1127. *In re Fritch*, 23 USPQ 2nd 1780, 1783-1784 (Fed. Cir. 1992). It is impermissible to use the claimed invention as an instruction manual or "template" to piece together the teachings of the prior art so that the claimed invention is rendered obvious. *In re Gorman*, 933 Fed. 2nd 982, 987, 18 USPQ 2nd 1885, 1888 (Fed. Cir. 1991). *In re Fritch*, 23 USPQ 2nd 1780 at 1784 (Fed. Cir. 1992).

The examiner's position that both the '214 and '376 each teach crosslinking of a maleic anhydride polymer is totally erroneous. The '214 patent discloses that maleic anhydride can be a starting material in the preparation of a water-absorbing polymer, but the anhydride groups are necessarily hydrolyzed to carboxylate groups because *all* of the '214 patent is directed to an aqueous polymerization. If not aqueous, no hydrogel is formed. In contrast, the '376 patent is directed solely to internal crosslinking of maleic anhydride polymers in a non-aqueous solvent or in the absence of a solvent. The "concept" of the '376 patent is no more than the teaching of internal crosslinking of a maleic anhydride polymer in the absence of an aqueous medium using a bicyclic amide acetal.

A person skilled in the art would have had no apparent reason or incentive to substitute the bicyclic amide acetal of the '376 patent for the 2-oxazolidinone of the '214 patent in a postcrosslinking step involving carboxyl groups. Such a substitution, after reading the '214 and '376 patents, would not have provided a reasonable expectation of successfully postcrosslinking water-absorbing particles.

The '214 patent teaches 2-oxazolidinone as a surface postcrosslinker and specifically discloses that the *more* reactive the surface postcrosslinkers provide the improved water-absorbing polymer particles. Therefore, the '214 provides no motivation or incentive to use bicyclic amide acetals of relatively low reactivity, as claimed, as a postcrosslinker.

The '376 patent does not overcome this deficiency. The '376 patent crosslinks a polymer via highly reactive anhydride groups. These groups are preserved for internal crosslinking by a bicyclic amide acetal by conducting the reaction in an inert solvent or in the absence of a solvent. The highly reactive anhydride groups are preserved to allow a reaction with the bicyclic amide acetal of relatively low reactivity to proceed. The polymers of the '214 patent contain *no* available anhydride groups for surface crosslinking. Water-absorbing

resins do *not* contain anhydride groups (i.e., maleic *anhydride* polymers are not water-absorbing), but rather contain substantially less reactive carboxyl groups. Accordingly, there is no reasonable expectation, and no logical reason or incentive for a person skilled in the art to consider using a bicyclic amide acetal as a postcrosslinking agent.

The examiner at paragraph 19 of the Office Action states that the '376 patent teaches a rapid and exothermic reaction, which implies that the bicyclic amide acetal is highly reactive. The examiner is incorrect. It is the anhydride that is highly reactive, not the bicyclic amide acetal. As stated above, and shown in Exhibit B, that is why the anhydride groups are hydrolyzed in water and are not present in a water-absorbing resin. The examiner's statement at page 19 is pure conjecture and unsupportable.

Overall, the cited combination of references teaches surface crosslinking using a highly reactive surface crosslinkers with a slow reacting carboxyl group ('214 patent) and crosslinking using a low reactivity bicyclic amide acetal to crosslink a highly reactive anhydride-containing polymer ('376 patent). In stark contrast, the present claims recite postcrosslinking of a low reactivity carboxyl group with a relatively low reactivity bicyclic amide acetal. Persons skilled in the art would have had no incentive to modify the '214 and '376 patents in this manner.

The presently claimed postcrosslinking process is neither taught nor considered by the cited references, alone or in combination, which in fact discourages such a process. A person skilled in the art simply would have had no reasonable expectation of successfully postcrosslinking a water-absorbing polymer using a bicyclic amide acetal after considering a combination of the '214 and '376 patents.

In addition, it could not have been predicted that a relatively inert bicyclic amide acetal, at a low weight percent, would successfully surface crosslink water-absorbing polymers having high absorption properties, as set forth in Examples 2-36 of the specification.


Accordingly, for all the reasons set forth above, it is submitted that the rejection of claims 1-8 as being obvious under 35 U.S.C. §103 over a combination of the '214 and '376 patent is in error and should be withdrawn.

In summary, it is submitted that all pending claims are in a form and scope for allowance. An early and favorable action on the merits is respectfully requested.

Should the examiner wish to discuss the foregoing, or any matter of form in an effort to advance this application toward allowance, the examiner is urged to telephone the undersigned at the indicated number.

Dated: March 8, 2010

Respectfully submitted,

By 

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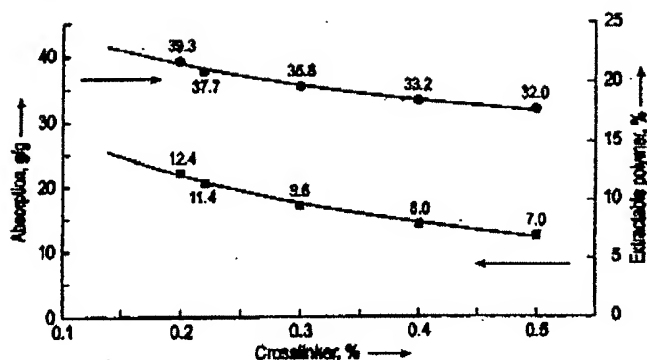


Figure 2. Centrifuge Retention Capacity (ERT 441.1-99) and extractable polymer (BRT 470.1-99) versus amount of crosslinker. The amount cross-linker relates to the content of acrylic acid.

5.1. Absorption Capacity

The absorption capacity of superabsorbents granules mainly depends on the density and homogeneity of the cross-linking of the polymer network, the number of charges on the polymer chains (degree of neutralization), and the ionic strength of the swelling. The higher the cross-linking density the lower the absorption and the lower the amount of extractable polymer (Fig. 2). The absorption capacity is usually determined gravimetrically.

Ionic effects have a strong influence on the absorption capacity. The higher the charge on the polymer chain (i.e., degree of neutralization) and the lower the ionic strength of the swelling liquid, the higher is the absorption (Figs. 3 and

4). Trivalent cations reduce the absorption more than bivalent cations, which in turn are more effective than monovalent cations. As substitute for urine either a synthetic urine solution or, more simply a 0.9 % salt solution is used. The way in which the test is performed also affects the determined degree of absorption. As the test system consists of superabsorbent granules, a part of the liquid is not fixed inside the superabsorbent particle itself but between the individual gel particles (interparticle or interstitial liquid). If this liquid is removed by centrifuging or brief application of a vacuum, the fluid retention of the superabsorbent itself is obtained.

A standard test for the absorption capacity is the centrifuged absorption capacity CRC (ERT 441.1-99) which is the ratio of the absorbed liq-

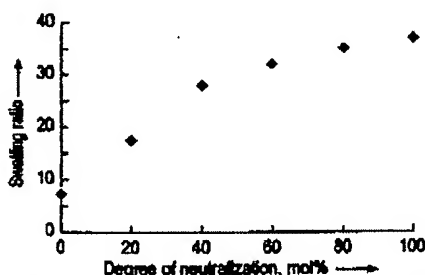


Figure 3. Swelling ratio versus degree of neutralization of a partially neutralized polyacrylate gel. The gel was neutralized after polymerization and swollen in a NaCl solution with a concentration of 153.8 mmol/L. Taken from the Y. Yin, Swelling Behavior of Polyelectrolyte Gels, Ph. D. Thesis, Princeton University 1993, p. 130.

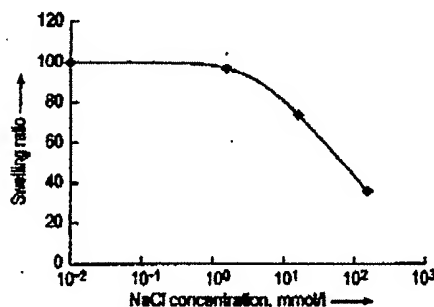


Figure 4. Swelling ratio versus NaCl concentration of the solution for a partially neutralized polyacrylate gel. The degree of neutralization was 80 %. Taken from the Y. Yin, Swelling Behavior of Polyelectrolyte Gels, Ph. D. Thesis, Princeton University 1993, p. 130.

uid to the mass of the dry superabsorbent. 0.2 g of superabsorbent granules are filled into a heat-sealable teabag, which is subsequently sealed. The teabag is weighed and then immersed in of 0.9 % NaCl solution for 30 min. Then it is transferred to a centrifuge (Fig. 5) and spun at 1600 rpm for 3 min, after which it is weighed again. The same procedure is carried out on a teabag without superabsorbent as a blank value. The retention is calculated from the weigh of the filled teabag after swelling and centrifugation m_1 , the weight of the dry superabsorbent filled into the teabag m_2 , and the weigh of the empty teabag after swelling and centrifugation m_3 .

$$CRC = \frac{m_1 - m_2 - m_3}{m_2} \quad (12)$$

5.2. Shear Modulus

The viscoelastic behavior of a substance is measured by subjecting it to a harmonically oscillating shear deformation γ . The shear modulus G is determined from the shear stress σ . The shear modulus G can be defined as a complex quantity [88]:

$$G = G' + iG'' \quad (13)$$

where G' is the storage modulus and is a measure for the elastically stored energy, whilst the loss modulus G'' represents the energy which is dissipated by viscous flow.

A definition of a gel in terms of dynamic mechanical properties is that the storage mod-

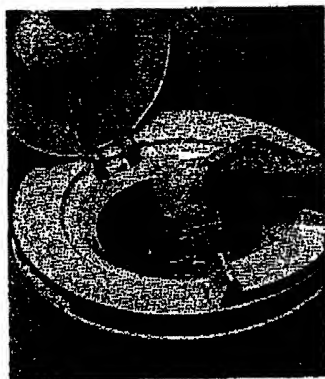


Figure 5. Centrifuge Retention Capacity (ERT 441.1-99)

ulus G' exhibits a pronounced plateau and the loss modulus G'' is considerably smaller than the storage modulus in the plateau region [89]. G' and G'' are measured with an oscillatory rheometer. Normally a plate-plate geometry is used. In practice, the pre-swelled superabsorbent granule is used. A defined grain fraction of the superabsorbent granule is pre-swelled to 70–90 % of the maximum swelling in 0.9 % NaCl solution. The pre-swelled granule is positioned on the lower plate. The gap between the plates is adjusted to the size of the gel particles. After lowering the upper plate, the gel particles which project over the edge of the plates are removed. An oscillating strain with a frequency of, e.g., 1 Hz is applied to one of the plates.

The swollen particles between the plates are in contact between each other. The shear modulus depends on the binding forces and the mobility between particles, and not only on the network structure of the gel. Therefore, the strain amplitude has to be very small, or measurements are carried out at different amplitudes and extrapolated to zero strain. Even then the method only gives meaningful results when the cross-linking density of the particles is not too low or high and when the particles are not surface-cross-linked. A more appropriate method is the use of a pre-formed disk of gel which fits perfectly into the gap between the plates of the rheometer. Such measurements [90] showed that in accordance with theory, the storage modulus increases with increasing cross-linker concentration (Fig. 6) or efficiency and with increasing monomer concentration in production. The

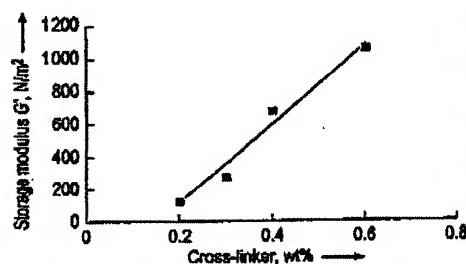


Figure 6. Storage modulus (frequency 1 Hz, amplitude 1 mrad) of sodium polyacrylate gels as a function of the amount of cross-linker used in polymerization. 1 g superabsorbent powder (300–600 μ m) was swollen in 50 mL of deionized water.

PREFACE

ADVANCED ORGANIC CHEMISTRY

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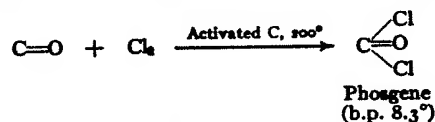
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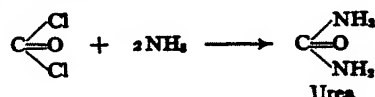
group is asymmetric have established that the group migrates with retention of configurations (Wallis, 1933; Wiberg,¹ 1956), perhaps because a cyclic transition state is involved.

11.27 Phosgene (COCl₂).— Phosgene was discovered by J. Davy (1812) as a product of the combination of carbon monoxide and chlorine under the influence of light (Gr. *phos*, light; L. *genere*, to be born), and it is now manufactured from these reagents with activated charcoal as catalyst. The substance

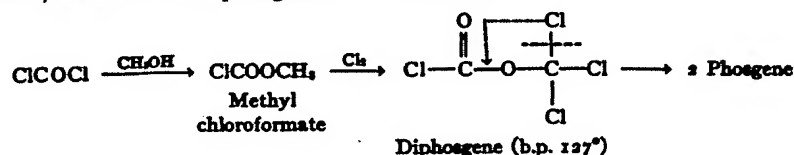


is a highly toxic gas having an odor resembling that of newmown hay; it is available in the liquefied form in steel cylinders.

Phosgene is the diacid chloride of the unstable carbonic acid and is sometimes called carbonyl chloride. It enters into typical reactions of hydrolysis to carbonic acid and ammonolysis to urea:



Phosgene was introduced as a war gas by the Germans in 1915 and was responsible for about 80% of the gas casualties in World War I. It is a lung irritant similar to chlorine but about ten times as toxic; it is also more insidious in action, since it gives no warning symptoms for an hour or two. The irritant action is attributed to hydrolysis in the tissues to hydrochloric acid, which is the agent directly toxic to cells. Phosgene is nonpersistent and hence applicable as an attacking agent. It is ineffective in wet weather as the result of ready hydrolysis, and it is stopped effectively by modern gas masks. The substance diphosgene is convertible into phosgene and has also been used as a war gas. It is trichloromethyl chloroformate, ClCOOCCl₂, and is made by chlorination of methyl chloroformate, derived from phosgene and methanol:


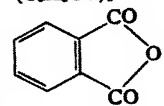


ANHYDRIDES

11.28 Properties.— With the exception of formic acid, which on dehydration yields carbon monoxide, the carboxylic acids form anhydrides in which water is eliminated between two molecules of the acid. Anhydrides of normal acids up to C₁₂ are liquids (Table 11.8); acetic anhydride is a mobile liquid

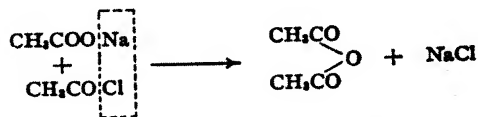
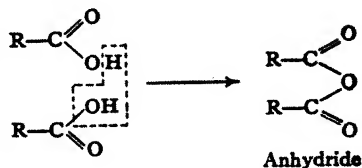
¹ Kenneth B. Wiberg, b. 1927 Brooklyn, N. Y.; Ph.D. Columbia (Doering); Univ. Washington; Yale Univ.

TABLE 11.8. ANHYDRIDES

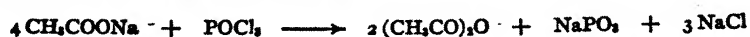
NAME	FORMULA	M.P., °C.	B.P., °C.	SP. GR.
Acetic anhydride	$(\text{CH}_3\text{CO})_2\text{O}$	-73	139.6	1.082
Propionic anhydride	$(\text{C}_2\text{H}_5\text{CO})_2\text{O}$	-45	168	1.012
<i>n</i> -Butyric anhydride	$(\text{n-C}_4\text{H}_9\text{CO})_2\text{O}$	-75	198	0.969
<i>n</i> -Valeric anhydride	$(\text{n-C}_5\text{H}_9\text{CO})_2\text{O}$		218 ^{74mm.}	.929
Stearic anhydride	$(\text{n-C}_{17}\text{H}_{35}\text{CO})_2\text{O}$	72		
Succinic anhydride		119.6	261	1.104
Benzoic anhydride	$(\text{C}_6\text{H}_5\text{CO})_2\text{O}$	42	360	1.199
Phthalic anhydride		132	284.5	1.527

with a pungent irritating odor. Anhydrides have nearly twice the molecular weights of the acids from which they are derived, and they boil at somewhat higher temperatures. Acetic anhydride (b.p. 139.6°, mol. wt. 102.09) boils at a higher temperature than esters, halogen compounds, and hydrocarbons of comparable weight.

11.29 Preparation.—A laboratory method of preparing acetic anhydride is the reaction of acetyl chloride with anhydrous sodium acetate (compare the Williamson synthesis of an ether). Several variations of this method

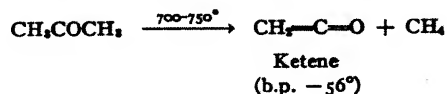


have been used; for example, when phosphorus oxychloride acts upon excess sodium acetate, acetyl chloride is formed, and this then reacts with more sodium acetate as above, the net result being:



Sulfur chloride is employed as the active halide in another procedure.

A modern industrial process for making acetic anhydride utilizes the highly unsaturated and reactive ketene, prepared by cracking acetone:



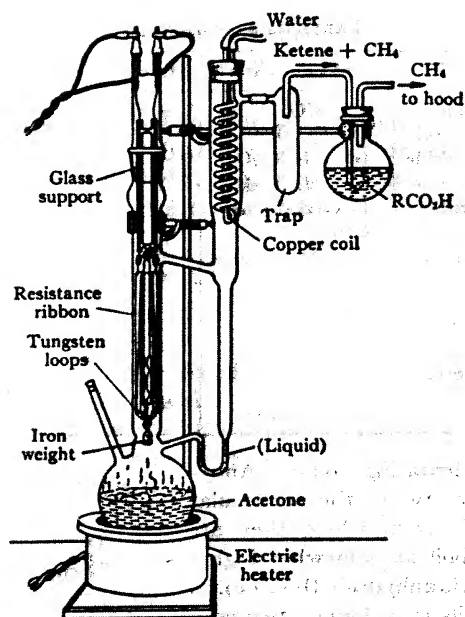
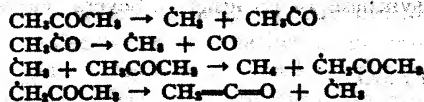


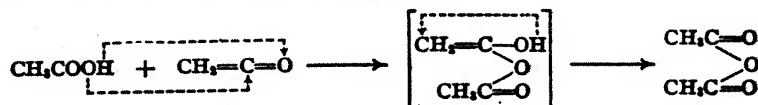
FIG. 11.1 — Ketene Generator

The reaction undoubtedly involves radicals and probably follows the path of thermal cracking of hydrocarbons (7.9) as suggested in the formulation. Cleavage

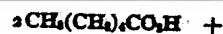


of a carbon-carbon bond gives methyl and acetyl radicals, and the acetyl radical can break down to carbon monoxide and another methyl radical. A methyl radical abstracts hydrogen from acetone to form methane and $\cdot\text{CH}_2\text{COCH}_3$, which then suffers β -fission to ketene and a methyl radical. Combination of two methyl radicals terminates the chain. A laboratory ketene generator is shown in Fig. 11.1. Refluxing acetone comes in contact with a glowing grid of resistance wire and undergoes cracking; unchanged acetone is condensed and returned to the boiling flask, and the ketene evolved in the gas stream along with methane is absorbed directly by a liquid reagent or in a solution.

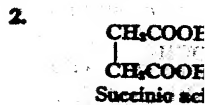
Ketene combines with most reagents containing either hydroxyl or amino groups; it reacts readily with acetic acid to give acetic anhydride, probably by addition to the carbonyl group and migration of the enolic hydrogen atom:



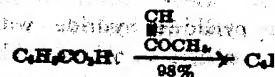
Mixed anhydrides of the higher acid, RCOOH , to unless the temperature is volatile acetic anhydride favoring rearrangement, into their anhydrides, for



Higher anhydrides that with either acetic anhydride and serves as a solvent for Example 2 illustrates the



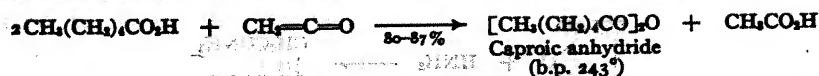
A method for conversions consists in reaction Arens, 1950). Wasserman



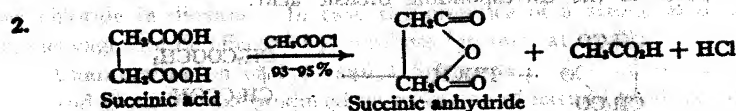
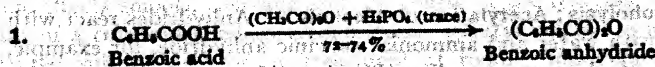
equivalent of methoxyacetyl vinyl benzoate (1) by opening mercuric benzoate to select Jones (1954) postulated that largely through the cyclic transition and Wasserman established adduct (1) with benzoic acid the anhydride and the ester

¹ Harry H. Wasserman, b. 19

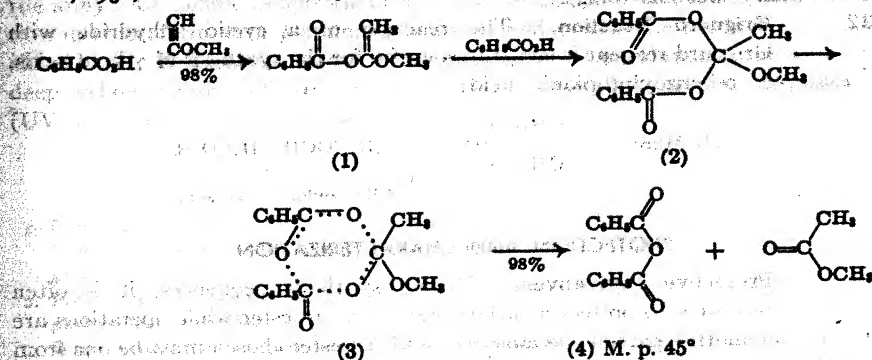
Mixed anhydrides of the type $\text{CH}_3\text{CO}\cdot\text{O}\cdot\text{COR}$ can be prepared by addition of a higher acid, RCOOH , to ketene and distillation at a greatly reduced pressure, but unless the temperature is kept low the mixed anhydride rearranges and the more volatile acetic anhydride distills first. By deliberate maintenance of a temperature favoring rearrangement, ketene can be employed for conversion of higher acids into their anhydrides, for example:



Higher anhydrides that are crystalline solids are prepared by heating the acid with either acetic anhydride or acetyl chloride; in either case acetic acid is formed and serves as a solvent from which the higher anhydride crystallizes on cooling. Example 2 illustrates the conversion of a dibasic acid into a cyclic anhydride.

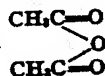


A method for conversion of an acid into its anhydride under very mild conditions consists in reaction with one half equivalent of methoxyacetylene (J. F. Arens, 1950). Wasserman¹ (1960) found that the reaction of benzoic acid with one



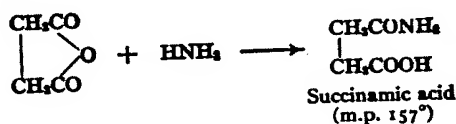
equivalent of methoxyacetylene can be controlled to permit isolation of *o*-methoxyvinyl benzoate (1) by operating at a low temperature with addition of a trace of mercuric benzoate to selectively catalyze addition to the triple bond. E. R. H. Jones (1954) postulated that the unstable orthoester (2) decomposes intramolecularly through the cyclic transition state (3) to the anhydride and methyl acetate, and Wasserman established that this indeed is the path: reaction of the mono-adduct (1) with benzoic acid- O^{18} resulted in equal distribution of isotope between the anhydride and the ester.

¹ Harry H. Wasserman, b. 1920 Boston, Mass.; Ph.D. Harvard (Woodward); Yale Univ.



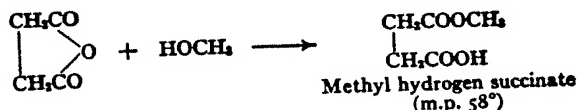
and the acetyl radical. A methyl radical and $\cdot\text{CH}_3\text{COCH}_3$. Combination of two methyl radicals is shown following grid of resistance and returned to the grid with methane is absent. Hydroxyl or amino radical, probably by hydrogen atom:

11.30 Hydrolysis and Ammonolysis. — Anhydrides are not so sensitive to water as acyl halides, but are more easily hydrolyzed than esters. Thus acetic anhydride can be hydrolyzed in a few minutes by boiling water. The anhydride dissolves in cold water to the extent of about 12 g. per 100 g., and if the solution is kept at room temperature, the substance undergoes complete hydrolysis only after an hour or two, whereas acetyl chloride is hydrolyzed at once.



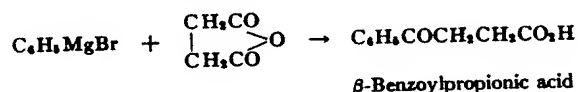
The reaction with ammonia parallels that with water and is used for preparation of the monoamides of dibasic acids.

11.31 Alcoholysis; Acetylation of Alcohols. — Anhydrides react with alcohol as with water and ammonia; succinic anhydride, for example, affords the monoester of the corresponding dibasic acid:



The most important application of the general reaction is acetylation of primary and secondary alcohols (8.23).

11.32 Grignard Reaction. — The reaction of a cyclic anhydride with Grignard reagent is sometimes useful for the synthesis of γ -keto acids, for example, β -benzoylpropionic acid:



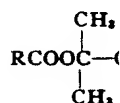
PROTECTION AND CHARACTERIZATION

11.33 Protective Derivatives. — During synthetic sequences, it is often necessary to protect a carboxyl group as an ester while operations are performed on another part of the molecule, and the ester chosen must be one from which the acid can be recovered without difficulty. Methyl and ethyl esters are satisfactory except in the case of a base-sensitive acid which will not withstand the fairly drastic conditions of alkaline hydrolysis. Benzyl esters are sometimes used to advantage since they can be cleaved by hydrogenation: $\text{RCO}_2\text{CH}_2\text{C}_6\text{H}_5 + 2\text{H} \rightarrow \text{RCO}_2\text{H} + \text{CH}_3\text{C}_6\text{H}_5$. They are also subject to acid cleavage under mild conditions.

Tetrahydropyranyl esters, useful as protective derivatives, are made by acid-catalyzed reaction of the acid with 2,3-dihydropyran at 20–30° (compare 8.38). They are cleaved by *p*-toluenesulfonic acid monohydrate in refluxing acetic acid.

The occasion may arise for preparation of a diacid monomethyl ester, the methyl tetrahydropyranyl group removed, the methyl ester group.

t-Butyl esters offer the advantages of the acid and isobutyl methods to the acid and isobutyl



Anhydrous *p*-toluenesulfonic acid anhydride effects smooth cleavage by means of a constant-pressure concentrated sulfuric acid or hydrogen chloride in dioxane. tionable, cleavage can be effected.

11.34 Characterization of and glutaric type

difficult to isolate or purify, either because a small amount of the pure acid is high melting. the anhydride (acetic anhydride) in chloroform with *p*-aminophenyl chloride (H. B. Henbest, 1955) deep yellow bands and are easily (UV and IR) facilitate identification.

1. Compare the acidity constants (K_a) of I , and Cl . What are the relative acidities?
2. Predict the relative order of the phthalic and isophthalic acid.
3. Write formulas for (a) 3,6-dimethylphthalic acid, (b) 3,6-dimethylisophthalic acid.
4. Which synthesis, Grignard or nitration, is more suitable for the synthesis of (a) $\text{CH}_3\text{CH}_2\text{CHBrCH}(\text{CH}_3)_2 \rightarrow \gamma$ -lactone, (b) $\text{CH}_3\text{CHOHCH}_2\text{CH}_2\text{Cl} \rightarrow \gamma$ -lactone?
5. Devise a synthesis of succinic anhydride from (a) $(\text{CH}_3)_2\text{CHCH}_2\text{COCl}$, (b) $(\text{CH}_3)_2\text{CHCH}_2\text{CO}_2\text{H}$.
6. How could $(\text{CH}_3)_2\text{CHCH}_2\text{COCl}$ be converted to (a) $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CO}_2\text{H}$, (b) $(\text{CH}_3)_2\text{CHCH}_2\text{CO}_2\text{H}$?
7. Outline a procedure for the isolation of *n*-amyl alcohol, *n*-amyl chloride, and *n*-amyl acetate from (a) $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CO}_2\text{H}$, (b) $(\text{CH}_3)_2\text{CHCH}_2\text{CO}_2\text{H}$.
8. What method of experimentation is most suitable for the identification of (a) $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CO}_2\text{H}$, (b) $(\text{CH}_3)_2\text{CHCH}_2\text{CO}_2\text{H}$?

MODERN SUPERABSORBENT POLYMER TECHNOLOGY

Edited by
Fredric L. Buchholz
Andrew T. Graham

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Preface

Acknowledgment

Contributors

1 Absorbency and

Fredric L. Buchholz

1.1. Absorbents

1.1.1. Traditional

1.1.2. Physically

1.2. Superabsorbents

1.2.1. Physically

1.2.2. Superabsorbents

1.2.2.1. Superabsorbents

1.2.2.2. Superabsorbents

1.2.2.3. Superabsorbents

1.3. Composite Absorbents

2 Chemistry of Superabsorbents

Thomas L. Staples, Jr.

2.1. Preparation of Superabsorbents

2.1.1. Example 1

Acrylic Acid

2.1.2. Example 2

Partial Emulsion

2.2. Free-Radical Polymerization

Related Monomers

2.2.1. Monomers

2.2.2. Storage

al absorbents may be dewatered by application of additional gravitational force. In a centrifuge, for example, dewatering may take place by overcoming the capillary pressure of the material. Resistance toward extra gravitational force requires very small capillaries, which have a large capillary pressure. However, for a fully saturated absorbent, any application of an accelerational force will cause some dewatering (see Eq. 1.1).

In summary, the absorbency of traditional materials is a function of the relative volume of open space in the sample (the porosity), the extent of connectedness of that volume, the size of the individual pores, and the mechanical strength of the porous structure, especially when wet. These factors are controlled by the choice of the structural material or fiber type, by the radius and length of the fibers and the pores, and by the method used to manufacture the absorbent structure.

1.2. SUPERABSORBENTS

1.2.1. Physics of Superabsorbents

Superabsorbent polymers are crosslinked networks of flexible polymer chains. The most efficient water absorbers are polymer networks that carry dissociated, ionic functional groups. A schematic drawing of such a network is shown in Figure 1.2. Except for the molecular-sized chains that make up the network, this picture of a network is remarkably similar looking to the mass of cotton fibers shown in Figure 1.1d. However, whereas traditional absorbents, like cotton, take up liquids by a flow

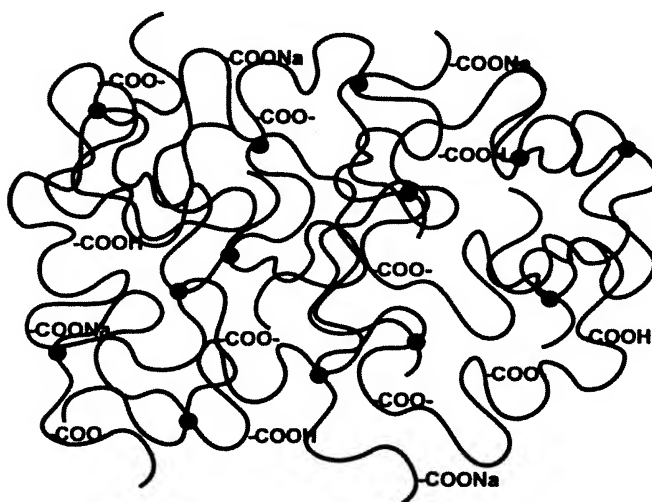


Figure 1.2. Schematic representation of a crosslinked polymer network. The dots represent the crosslinks between the coiled polymer chains, which have ionic carboxylate functional groups spaced along their length.

or convective nism. Diffusion nonorganized makes the movement faster rate. The position in space

Water movement is initial. The particle, the sorbent polymer, the water molecules of water, the particle of superabsorbent cause polymer more slowly. The motion of the particle in the water in each direction, the each polymer motion is motion and the

The polymer depends on the constant, random superabsorbent the chain elongation. At first, the particle, the movement from the elongation



Figure 1.3. Water particle. Magnified view.

or convective mechanism, superabsorbents function by means of a diffusive mechanism. Diffusion is a molecular phenomenon wherein molecules move in a random, nonorganized manner as a result of their thermal energy. Increasing the temperature makes the molecules move faster, and the diffusive processes occur therefore at a faster rate. The molecules are in constant motion and will move from their average position in space toward regions of lower activity by purely statistical means.

Water moves into a particle of superabsorbent polymer because the activity of water is initially lower in the interior of the particle. As water diffuses into the particle, the particle volume increases and the polymer chains that form the superabsorbent polymer network must also move, generally in a direction opposite to that of the water molecules, in order to accommodate the volume of the additional molecules of water. The change in volume is apparent in Figure 1.3, which shows a particle of superabsorbent polymer before and after swelling in a dilute salt solution. Because polymer molecules are much larger than water molecules, they diffuse much more slowly. Not only are the polymer molecules larger, but they are also connected one to the other by the crosslinks, so that the polymer does not eventually dissolve in the water and become useless as a superabsorbent. Therefore, to move in a certain direction, the polymer chains must move cooperatively, requiring more time than if each polymer chain, or each monomer segment, moved individually. The slow polymer motion is a principal rate-limiting phenomenon in polymer swelling. This slow motion and the factors that affect it are discussed more fully in Chapter 5.

The polymer chains each have a preferred size and orientation in space that depends on their environment and their own thermal motion, which keeps them in constant, random motion about an average location. When water diffuses into the superabsorbent polymer, the favored, random configuration is disturbed, because the chain elongates as a necessary consequence of the change in volume of the particle. At first the disturbance is not very large, but as more water diffuses into the particle, the magnitude of the disturbance increases. Eventually, the force resulting from the elongation of the polymer chains balances the force that results from the

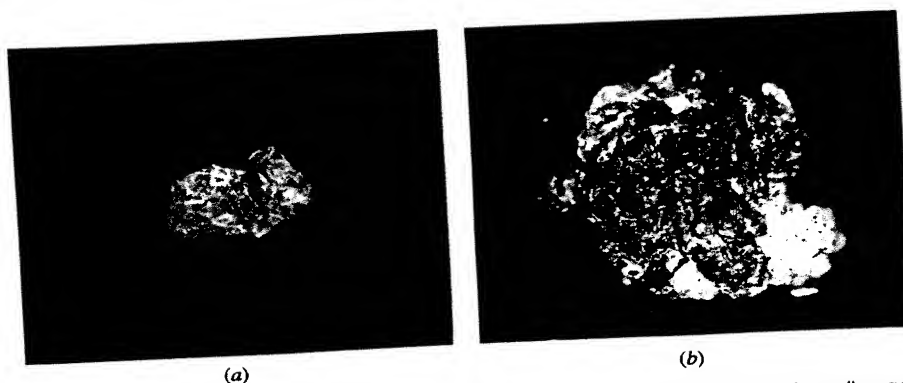


Figure 1.3. Water absorption by superabsorbent polymer: (a) dry granule and (b) swollen gel particle. Magnifications $\times 25$.

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e requires very
a fully saturat-
ome dewatering

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connectedness of
strength of the
by the choice of
e fibers and the
re.

mer chains. The
dissociated, ionic
wn in Figure 1.2.
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liquids by a flow



k. The dots represent
carboxylate functional

CHEMISTRY OF SUPERABSORBENT POLYACRYLATES

Thomas L. Staples, David E. Henton, Fredric L. Buchholz

Among the absorbent and superabsorbent polymer types described in Chapter 1, the crosslinked, partially neutralized poly(acrylic acids) are the principal superabsorbent polymer of commerce. Numerous other polymers have been crosslinked to form water-swellaable gels, but no other polymer can provide the high charge-to-mass ratio as economically as poly(sodium acrylate). For this reason, this chapter on the chemistry of superabsorbent polymers is restricted to the formation of crosslinked networks of poly(acrylic acid) and its salts.

General descriptions of other absorbent and superabsorbent polymer types are available in the literature. Gels of some of the cellulose-based, water-swellaable polymers, such as sodium carboxymethylcellulose, are described by Doelker.¹ Alginate gels are described by Segeren et al.² and Aslani and Kennedy³ and in the numerous references therein. Other biopolymer gels have been described by Clark and Ross-Murphy⁴ and Clark.⁵ Hydrogels of poly(vinyl alcohol) are reviewed by Peppas,⁶ and those of poly(ethylene oxide) are reviewed by Graham⁷ and Apicella et al.⁸ More extensive discussions of these and other alternatives to polyacrylate absorbents may be found in Chapter 6.

To introduce the descriptive chemistry of superabsorbent polymers, we first present two example polymerizations. Polymerization kinetics are then discussed in some detail, illustrating how process conditions affect the structure of the polymer

network. Our study of the polymerization kinetics has been aided by some new experimental techniques, which are also described. Crosslinking via both co-polymerization and post-polymerization reactions is covered, and brief mention is made of kinetic modeling as it may apply to superabsorbents.

2.1. PREPARATION OF SUPERABSORBENT POLYACRYLATES

Superabsorbent polyacrylates are prepared by free-radical initiated polymerization of acrylic acid and its salts, with a crosslinker, in aqueous solution or as a suspension of drops of aqueous solution in a hydrocarbon. The polymerization chemistry is shown schematically in Figure 2.1. The two principal processes, bulk solution polymerization and suspension polymerization, share many features. The monomer and crosslinker concentrations, the initiator type and concentration, polymerization modifiers, the relative reactivities of the monomers, the basic polymerization kinetics, and the reaction temperature are all significant factors in both processes.

In either process, the monomers are dissolved in water at concentrations of 20–40 wt%, and the polymerization is initiated by free radicals in the aqueous phase. Several types of free-radical sources may be used, including thermally decomposable initiators, redox systems, photochemical initiators, and combinations of them. Redox systems used for the crosslinking copolymerizations include couples of persulfate/bisulfite, persulfate/thiosulfate, persulfate/ascorbate, and hydrogen peroxide/ascorbate. Thermal initiators include persulfates, 2,2'-azobis(2-amidinopropane)-dihydrochloride, and 2,2'-azobis(4-cyanopentanoic acid). Combinations of initiators are used especially when the polymerization takes place over a broad temperature range.

The monomers are polymerized either in the acid form (pH 2–4) or as the par-

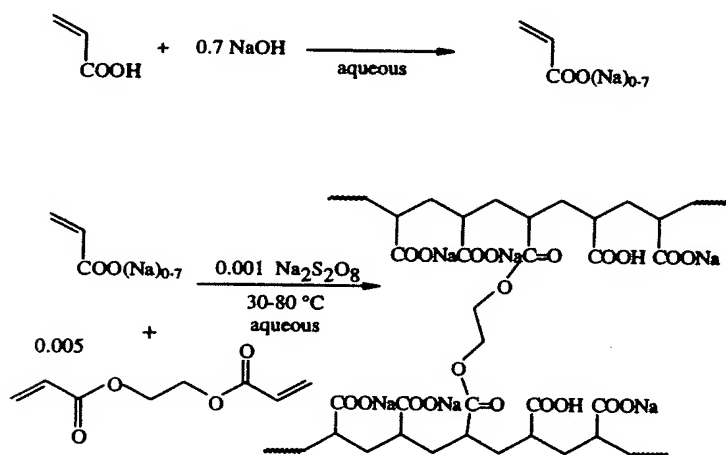


Figure 2.1. Schematic depiction of the chemistry of polymerization of superabsorbent poly(acrylates).

tially neutral sodium carboxylate. On consideration of the ability of the monomer to be neutralized, it is evident that the monomers made from monomers a

Small amounts of superabsorbent polymer and allyl methacrylate, propanetriol, tetraallyloxy addition to the double bond affects the amount of its relative ring will also double bond reaction reactor monomer mi

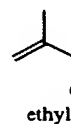


Figure 2.2. The structure of superabsorbent poly(acrylates).

tially neutralized salt (pH 5–7). Inexpensive bases, such as sodium hydroxide and sodium carbonate, are used as neutralizing agents. A choice would be made based on consideration of the pH of the base solution and the resulting potential for hydrolyzing the crosslinker, the solubility limits of the base in water and on the solubility of the monomer salt in water. In suspension polymerizations, the acrylic acid must be neutralized prior to polymerization because of a substantial partition coefficient of acrylic acid in the liquid hydrocarbons used as continuous phase. The polymers made from acrylic acid (and neutralized later) or from the partially neutralized monomer are somewhat different because of the presence or absence of charged monomers and polymers during the formation of the polymer network.⁹

Small amounts of crosslinkers play a major role in modifying the properties of superabsorbent polymers. The co-polymerizable crosslinkers used in superabsorbent polymers range from di-functional compounds, such as diacrylate esters and allylmethacrylate, to tri-functional compounds, such as 1,1,1-trimethylolpropanetriacrylate and triallylamine, and to tetra-functional compounds, such as tetraallyloxyethane. The structures of these substances are shown in Figure 2.2. In addition to modifying the swelling and mechanical properties, the crosslinker affects the amount of soluble polymer formed during the polymerization as a result of its relative reactivity with acrylic acid or sodium acrylate. Efficiency of crosslinking will also depend on steric hindrance and reduced mobility at the site of pendent double bonds, the tendency of a given crosslinker to undergo intermolecular addition reactions (cyclopolymerization), and the solubility of the crosslinker in the monomer mixture. As a result of each of the above variables, a number of polymer-

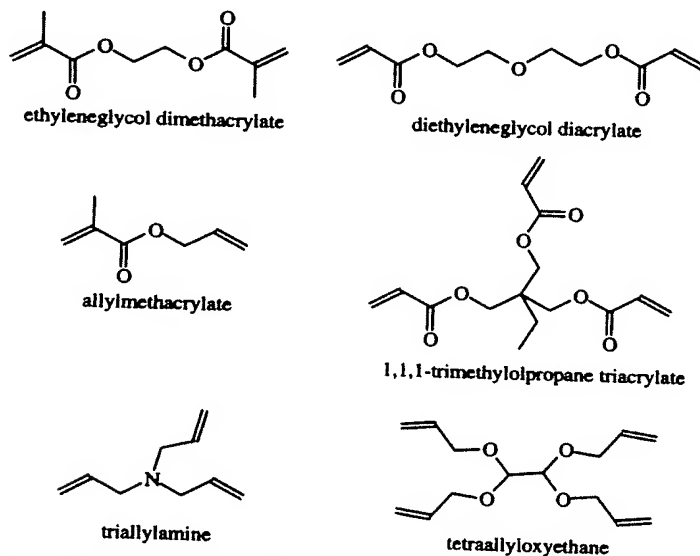


Figure 2.2. The structure of vinyl crosslinkers commonly used in the polymerization of superabsorbent poly(acrylates).

ization additives are also used to ameliorate processing difficulties on a large scale. These additives are not discussed here, because they typically have little effect on the basic chemistry. To describe the synthesis of superabsorbent polymer in a little more detail, two typical synthetic procedures are given below.

2.1.1. Example 1: Crosslinking Co-Polymerization of Acrylic Acid

The polymerization reactor is assembled from a 1-L resin reaction kettle, stoppers, polyethylene tubing, and a thermocouple, as shown in Figure 2.3. The reactor contents may be stirred by means of either a magnetic stirrer (3.2-cm PTFE-coated stir bar) or a bladed agitator on a glass or stainless steel shaft. The monomer solution is prepared in the reactor by mixing 250 g acrylic acid, 600 g distilled water, 0.20 g ethylenediaminetetraacetic acid, and 2 g ethylene diacrylate. The monomer solution is agitated and deoxygenated with nitrogen gas bubbled through the solution at a flow rate of 400 cm³/min for 60 min.

When the requisite deoxygenation time has passed, the initiator solutions are added to the stirred monomer solution, using pipettes or syringes, in the order list-

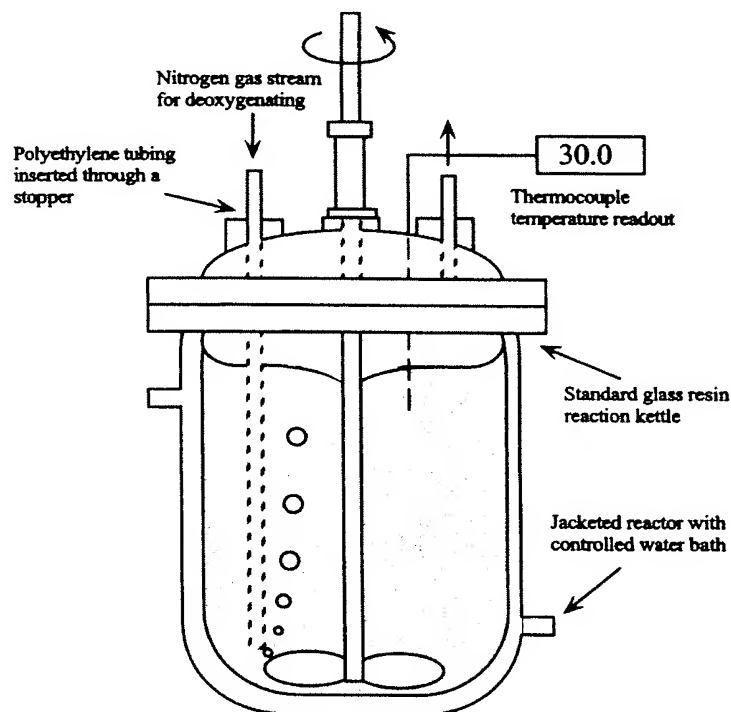


Figure 2.3. Schematic of a reactor suitable for laboratory polymerizations.

ed: 5 cm³ of a 1
ous solution of
sodium thiosulfate

An exothermic
was adequately
reaction has sub
tents may be co
moved from the
tween the glass
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eral pieces by h
The crumbled n
carbonate disso
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a snapping and
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gel is spread or
crushed or grou
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2.1.2. Example 2: Neutralized Acrylic Acid

The same polym
of 250 g acryl
crosslinking ag
crosslinker is di
which is a 40%
Dow Chemical
alcohol) (Air Pr
tion. The acrylic
adding a sodium
tilled water. The
the solution.

The monome
tor solutions are
sodium persulfa
merization begi
nearly adiabatic
the reactor con
monomers. The
hand and grou
crushed to the d

The polymer
superabsorbent

tions are selected to minimize
ons, their handling and disposi-
at superabsorbent manufactur-
fraction needs to be managed.
ie product by screening. That,
with them. Two paths are dis-

a second product or to include
84-89 This path is not discussed
erabsorbent fines into the pri-
ater, and fresh gel (direct from
uniform blended product.^{14,15}
ied product, are blended. Fines
without substantial agglomera-
followed by mixing of the hydrat-
cribed for the addition of reac-
) Also, recycle of fines to a gel
ized), and a few parts of water
ure of hydrated fines and fresh
l into "shapes having sufficient

d fines and the gel, for example
ether, the fines are not chemi-
the product may not retain its
ition." Viewing the swelling of
at the agglomerated larger par-
nass swells.

ation step is also described. In
omer solution and the mixture
first added to the reactor, fol-
y of the monomer mix increas-
rticular problems were noted.
bed in these patents. However,
might be useful at a commer-
ns containing fines¹⁶ is similar
en polymerizing on a continu-
a part of the monomer mix.²⁹
ling solvent, a nonswelling salt
acid and then added to an aque-
an be added may be as high as
ess.^{16,17,29} When fines are recy-
arly equivalent to properties of
a case for polymers of the same
rder load was noted.¹⁷

3.2.8. Addition of Post-Treatments

3.2.8.1. Advanced Products. The processes described above produce a parti-
cle with crosslinking that may be assumed to be essentially uniform throughout the
particle. As such, the swelling and modulus behavior of the product particles can be
described by theories of network swelling and elasticity (see Chapter 5). One prob-
lem associated with these superabsorbent polymers was also recognized in a variety
of water soluble polymers, e.g., poly(acrylamide), cellulose ethers,⁹⁵ or soluble
poly(acrylic acid).⁹⁶ This problem is the tendency of the granular polymers to
clump, "gel block," or form fish-eyes when aqueous liquids are added to them or
they are added to aqueous liquids. The surfaces of the massed particles swell rapid-
ly to form a soft, deformable layer. The resulting particle deformation and interpar-
ticle adhesion reduces interparticle porosity and limits the swelling rate of the poly-
mer mass to the diffusion rate of liquid through the partially swollen mass.

The first attempts to solve this problem in highly absorbent anionic polyelec-
trolytes used multivalent cations to form a crosslinked surface layer that was more
rigid than the original core polymer.⁹⁷ Subsequently, to give products with improved
dispersibility and absorption rate, the surface of crosslinked polyacrylate particles
was reacted with a variety of multifunctional organic compounds.^{49,50,98,99} This
structural improvement is shown schematically in Figure 3.9. Swelling capacity
data as a function of particle size readily demonstrate that a shell of real, as opposed
to infinitesimal, thickness is formed by surface crosslinking processes. The shell of
higher crosslink density provides a more rigid surface layer during swelling and pre-
vents the gel-blocking that would otherwise occur early in the swelling process
(Chapter 5). As a result, liquid can flow through the bed of particles to each particle,
increasing the effective surface area available for swelling and the apparent swelling
rate. The swelling and modulus behavior of structured particles are discussed in
Chapter 5.

Because a surface layer is formed on each individual particle, the crosslinking
reaction, but not necessarily the reagent addition, must occur after achieving the de-
sired particle size distribution. Any compound that can react with two or more func-
tional groups on the polymer backbone can function as a surface crosslinking
reagent. For superabsorbents, this requires reagents that can react with the car-

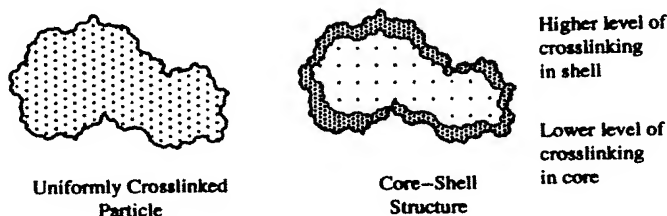


Figure 3.9. Schematic representation of a uniformly crosslinked superabsorbent particle and a structured particle with a surface layer of higher crosslink density.

boxylic acid or carboxylate moieties on separate, adjacent polymer chains. Quaternary amines have been used,¹⁰⁰ but the most common reagents add surface crosslink density as a result of formation of ester crosslinks. These surface crosslinking agents include polyhydric alcohols,^{49,50} glycidyl compounds,¹⁰¹⁻¹⁰³ and alkylene carbonates.¹⁰⁴

Blenders suitable for the addition of surface crosslinking agents include screw mixers, ribbon mixers, fluidized beds,⁴⁹ high-speed rotating paddle mixers,^{50,90} vortex mixers, rolling mixers, or double screw mixers.¹⁰⁴ Spraying the surface crosslinking reagent into the blender, using small droplet sizes, preferably less than 300 μm , helps reduce the amount of liquid required to disperse the surface crosslinking reagent.⁵⁰ A high-speed paddle mixer used for this process operates at greater than about 600 m/min of a lead-end peripheral speed.⁹⁰ In one example, a Turbulizer, produced by Hoskawa Micron K. K., was operated at 3,000 rpm. The inner surface of the mixer is preferably coated with a material that minimizes adhesion of the wetted polymer to the walls of the mixer, for example, polypropylene or a poly(tetrafluoroethylene) resin. When a high-speed mixer is used, the amount of organic solvent used to help disperse the surface crosslinking reagent may be minimized or even completely eliminated.

A heating step is normally necessary for the reaction of surface crosslinking agents with the partially neutralized poly(acrylic acid) backbone. The time and temperature of heat treatment are chosen, considering the reactivity of the crosslinking reagent, to give the desired end-use properties. Naturally, longer reaction times and higher temperatures increase, for a reagent of any reactivity, the extent of reaction. Tsubakimoto et al.,⁵⁰ claim temperatures of 90°–300°C while Dahmen and Mertens¹⁰⁴ teach 150°–300°C. However, at temperatures greater than about 250°C, degradation of the polyacrylate by oxidation or decarboxylation may become significant (see Chapter 2, Section 2.5.4.2). More specifically, the reactive epoxy groups in ethylene glycol diglycidyl ether react in 30 min at 140°C.¹⁰⁵ The less reactive ethylene carbonate requires 1 h at 180°C or 15 min at 215°C.¹⁰⁴

Suitable heating devices include fluidized-bed dryers, infrared dryers, agitated-trough dryers,⁴⁹ paddle dryers,⁵⁰ vortex dryers, or rotating-disc dryers.¹⁰⁴ Comparative data that would allow the selection of the most suitable device are not given. Both direct-contact dryers (rotating-disc dryers, paddle dryers) and fluidized-bed dryers are used commercially to provide heat for the reaction step. Direct-contact dryers deliver heat to the polymer particles by contact of the particles with a hot surface, while fluidized-bed dryers deliver heat to the particles with a stream of hot air of high enough velocity to suspend the particles in the airstream. Direct-contact dryers, for this application, must be designed keeping in mind the possibility of attrition of the particle surface (from the mechanical action of the paddles or other movable surfaces on the particles) and consequent degradation in product properties. The air-handling equipment associated with fluidized-bed dryers may make them expensive to operate.

Initially, structured particle technology was viewed as solving the problem of gel-blocking, as measured by a fish-eye test⁴⁹ or a similar test conducted without a compressive load. These early tests were only able to qualitatively distinguish be-

tween structured polyacrylate, Tsubakimoto crosslinking reagent; when the reagent is a carbonate (see section 4.6.4) that may be used (load) were able to qualify under different sets of conditions of the reagent introduction over the surface, indicating success in the absence of a compressive load.

Optimization of the process for sorbency under load requires the use of crosslinking reagents as alcohol or aqueous solutions with these approaches. The reaction temperature of the surface crosslinking agent and the water cause the polyacrylates, such as silica, to be more reactive. The absence of the treatment of the reagents with the process.^{50,90} The alcohol agents over the powder or prevent agglomeration. The use of air recovery and recycle require extra equipment.

Adding 0.2 wt% neutralized polyacrylate to the effect of reagent penetration. Twenty-five grams of a dish for 15 min at 215°C as a heat sink (Chapter 4, section 4.6.4.2) data. Solution increases. The ethyleneglycol diglycidyl ether reagent. This has been used to add reagent into the particles rather than just on the surface.

Other process changes for glycerol the optimum on the values of swelling may be reduced by increasing the salt concentration.

nt polymer chains. Quater-
gents add surface crosslink
these surface crosslinking
ounds,¹⁰¹⁻¹⁰³ and alkylene

inking agents include screw
ing paddle mixers,^{50,90} vor-
.¹⁰⁴ Spraying the surface
t sizes, preferably less than
d to disperse the surface
for this process operates at
speed.⁹⁰ In one example, a
rated at 3,000 rpm. The in-
terial that minimizes adhe-
example, polypropylene or
ixer is used, the amount of
inking reagent may be mini-

on of surface crosslinking
backbone. The time and tem-
activity of the crosslinking
4, longer reaction times and
vity, the extent of reaction.
30°C while Dahmen and
greater than about 250°C,
ylation may become signif-
the reactive epoxy groups
°C.¹⁰⁵ The less reactive eth-
C.¹⁰⁴

s, infrared dryers, agitated-
ig-disc dryers.¹⁰⁴ Compara-
table device are not given.
dryers) and fluidized-bed
action step. Direct-contact
the particles with a hot sur-
cles with a stream of hot air
e airstream. Direct-contact
mind the possibility of at-
ion of the paddles or other
radiation in product proper-
ized-bed dryers may make

as solving the problem of
ar test conducted without a
qualitatively distinguish be-

tween structured polymers made under different sets of process conditions. For ex-
ample, Tsubakimoto et al.⁵⁰ showed that a water/alcohol carrier for the surface
crosslinking reagent yields a structured polymer with less fish-eye formation than
when the reagent is added undiluted. Later, more sophisticated tests (see Chapter 4,
section 4.6.4) that measure swelling under a compressive load (absorbency under
load) were able to quantitatively distinguish between structured polymers made un-
der different sets of process conditions. Results of these tests suggest that penetra-
tion of the reagent into the particles and control of the dispersion of the crosslinking
agent over the surface of the particles are critical process considerations for achiev-
ing success in the absorbency under load test.

Optimization of the surface crosslinking process to reduce gel-blocking in an ab-
sorbency under load test has been addressed in a number of ways. Surface
crosslinking reagents have been added in aqueous solutions and other diluents such
as alcohol or aqueous salt solutions.^{102,103} However, there are several difficulties
with these approaches.¹⁰⁶ Water swells the particle surface and lowers the glass tran-
sition temperature of the polymer at the surface, increasing penetration of the sur-
face crosslinking agent into the polymer particle. However, excessive amounts of
water cause the polymer to swell and can make handling difficult. Inorganic partic-
ulates, such as silicates, in addition to controlling the hydrophilic/hydrophobic bal-
ance of the treatment reagent, are used, in combination with high-speed blending of
the reagents with the polymer, to control agglomeration during the reagent addition
process.^{50,90} The alcohol or salt solution helps disperse the surface crosslinking
agents over the powder by diluting the crosslinker (larger volume) and helps control
or prevent agglomeration of the powder by reducing the activity of water in the so-
lution. The use of an organic solvent has the obvious disadvantage of requiring re-
covery and recycle. Also, for example with the lower alcohols, the low flash points
require extra equipment and more safeguards to maintain safe operation.

Adding 0.2 wt% glycerol, in combinations of water and *n*-propanol, to a 65%
neutralized polyacrylate made by the process of Siddall and Johnson²⁸ shows the ef-
fect of reagent penetration. One gram of liquid was added to 100 g of polymer pow-
der. Twenty-five grams of the reagent treated polymers was heated in an aluminum
dish for 15 min at 200°C in a preheated circulating-air oven equipped with a steel
plate as a heat sink. Table 3.5 shows the swelling capacity (method described in
Chapter 4, section 4.6.1.2) and absorbency under load (described in Chapter 4, sec-
tion 4.6.4.2) data. Swelling capacity decreases as the amount of water in the reagent
solution increases. Similar results have been obtained by using aluminum acetate,
ethyleneglycol diglycidyl ether, or ethylene carbonate as the surface crosslinking
reagent. This has been interpreted as resulting from increased penetration of the
reagent into the particle and increased crosslinking throughout the particle rather
than just on the surface.

Other process choices also affect the resulting properties. Table 3.5 suggests that
for glycerol the optimum weight ratio of water to *n*-propanol is about 30:70 (based
on the values of swelling capacity and absorbency under load). The amount of water
may be reduced by choosing a more hydrophilic organic solvent such as methanol.
Increasing the salt concentration of the crosslinker solution also decreases the hy-

Table 3.5. The effect of solvent hydrophilicity on the properties resulting from surface crosslinking of a polyacrylate treated with 0.2 wt% glycerol and then heated at 200°C for 15 min

Solvent Composition Water/ <i>n</i> -propanol (w/w)	Swelling Capacity (g/g)	Absorbency Under 2.0 kPa Load (g/g)
Starting material	39.0	9.0
0/100	36.4	23.2
10/90	35.0	21.6
20/80	34.7	29.0
30/70	28.8	29.3
40/60	30.5	29.3
50/50	29.3	28.6

drophilicity of the solution (reduced particle surface swelling) and has the expected effect on product quality. The amount of crosslinker solution and the concentration of crosslinker in the solution also impact the results. When too little crosslinker solution is used, for example to avoid agglomeration, the particle surface coverage can be incomplete, leading to increased gel-blocking in the swelling under load tests. When the concentration of crosslinker is too low, or an insufficient quantity of reagent is applied, the amount of additional crosslinking at the surface does not make the surface sufficiently rigid to give the required resistance to gel-blocking.

More recently, the desire for products with an improved combination of swelling capacity and absorption under load^{107,108} has led to more complex surface crosslinking systems.^{100,106,109} In one case,¹⁰⁰ a shell structure is achieved by using two surface crosslinking reagents with different solubility parameters, one greater than 12.5 (cal/g³)^{1/2} and the other less than 12.5 (cal/g³)^{1/2}. The combination of solubility parameter and low molecular weight of the crosslinking reagents (less than 350 g/mol) is said to optimize the penetration of the surface crosslinking reagent into the particle (compare row 4 to rows 2 and 3 of Table 3.6). In a second case, surface crosslinking with a specific class of high-molecular-weight (greater than 1,000 g/mol) azetidinium compounds leads to polymer particles with more ideal shell thicknesses (less than 10% of the particle radius).¹⁰⁹ The high molecular weight of the reagent limits the penetration of the crosslinking agent into the particle so that the swelling capacity is not reduced too greatly. A range of surface tension, about 40–50 dynes/cm, of the applied crosslinker solution promotes spreading of the crosslinker solution over the surface of the particles.¹¹⁰ A two-step addition of surface crosslinking agent also leads to improved properties.¹¹¹ Another two-part process, in which a first crosslinker (hydrophilic polymer or metallic compound) is reacted with a second additive on the surface of a wet polymer (10–100 parts), has also been described. The extent of hydration of the polymer and crosslinker are chosen to give the desired penetration of the surface crosslinking reagents into the particle and the desired combination of properties. The process seems most suitable for suspension-made polymers, but its inventors claim its utility is for polymers made by solution polymerization. In one example, a coating of poly(ethyleneimine)

Table 3.6. A comparison of making structured

Reagent
Aluminum acetate
Glycerol
EGDGE ^a
Glycerol/EGDGE
(process of Date et al. ¹⁰⁹)
Ethylene carbonate
Example 1 of Brehm and Hartan ¹¹¹
Process of Burgert et al. ¹¹²

^aEthyleneglycol diglycidyl ether.^bMethod of Chapter 4.8.^cMethod of Chapter 4.8.

crosslinked with a resin with "excellent" properties. This process is said to be a "one-step" reaction.

Despite the differing results, the differences in swelling capacity are produced with the same crosslinking reagent. The reagent is a neutralized poly(acrylic acid) chosen to give the desired swelling capacity (35 g/g). The data in the indicated table are from the indicated source.

The surface crosslinking process produces similar results under load as surface crosslinking. Even surface crosslinking process. Some of the conditions, such as 2, section 2.7. However, it is noted that the crosslinking of a structured particle, such as a factor. The

ies resulting from surface
and then heated at 200°C

Absorbency Under 2.0 kPa Load (g/g)
9.0
23.2
21.6
29.0
29.3
29.3
28.6

ling) and has the expected
tion and the concentration
m too little crosslinker so-
rticle surface coverage can
swelling under load tests.
n insufficient quantity of
g at the surface does not
sistance to gel-blocking.
d combination of swelling
more complex surface
cture is achieved by using
ty parameters, one greater
2. The combination of sol-
linking reagents (less than
rface crosslinking reagent
3.6). In a second case, sur-
weight (greater than 1,000
les with more ideal shell
high molecular weight of
nt into the particle so that
of surface tension, about
romotes spreading of the
A two-step addition of sur-
rties.¹¹¹ Another two-part
r or metallic compound) is
polymer (10–100 parts), has
er and crosslinker are cho-
king reagents into the par-
ss seems most suitable for
tility is for polymers made
g of poly(ethyleneimine)

Table 3.6. A comparison of properties resulting from "optimum" process conditions for making structured particles

Reagent	Swelling Capacity ^b Before Treatment (g/g)	Swelling Capacity (g/g)	Absorbency Under Load ^c (g/g)		
			2.0 kPa	3.9 kPa	6.2 kPa
Aluminum acetate	39	35	25	18	—
Glycerol	39	35	33	21	12
EGDGE ^a	40	35	35	31	24
Glycerol/EGDGE (process of Date et al. ¹⁰⁹)	45	35	35	31	26
Ethylene carbonate	50	36	30	25	21
Example 1 of Brehm and Hartan ¹¹¹	40	36	33	25	21
Process of Burgert et al. ¹¹²	39	36	32	26	22

^aEthyleneglycol diglycidyl ether.

^bMethod of Chapter 4 Section 4.6.1.2.

^cMethod of Chapter 4 Section 4.6.4.2.

crosslinked with a polyglycerol polyglycidyl ether resulted in a superabsorbent resin with "excellent" stability (by which the inventors seem to mean gel modulus). This process is said to require less stringent temperature control to achieve adequate reaction.

Despite the differences in the various surface crosslinking reagents and the resulting differences in reaction conditions, products with very similar properties may be produced with a variety of surface crosslinking processes. Table 3.6 shows swelling capacity and absorbency under load results when a variety of surface crosslinking reagents were applied in a methanol/water solvent system to a 65% neutralized poly(acrylic acid). The reaction conditions (temperature and time) were chosen to give the highest values of absorbency under load at the target swelling capacity (35 g/g). The choices were based on our experience with these processes and on data in the indicated references.

The surface crosslinking process of Brehm and Hartan¹¹¹ and the alternate structured particle technology of Burgert et al.¹¹² (discussed in more detail below) also produce similar results (last two rows of Table 3.6). In each case, the absorbency under load was substantially improved compared with the material before surface crosslinking. Even so, property differences remain that depend on the individual surface crosslinking reagents or process, despite our attempts to optimize the process. Some of these may result from insufficient optimization of the process conditions, such as spreading of the reagent, or chemistry, as discussed in Chapter 2, section 2.7. However, a consideration of the several reagents leads to the speculation that the crosslinker structure might also be a factor in the performance of the structured particle. The distance between functional groups in the crosslinker might be such a factor. This is a question that needs to be resolved by future study.

Improved properties have also been achieved by forming a structured particle in a different way. Polymers made with certain crosslinkers or combinations of crosslinkers and heated in the presence of special oxidizing agents have dramatically improved absorbency under load and swelling capacity.¹¹² In this technology, all necessary ingredients are added prior to polymerization so that they are mixed uniformly in the resulting particles. A variety of primary crosslinkers may be used alone or in combination with a secondary crosslinker, also uniformly distributed throughout the particle. Primary crosslinkers that have been used include 1,1,1-trimethylolpropane triacrylate (TMPTA), ethoxylated TMPTA, allyl methacrylate, and various diacrylates and methacrylates based on poly(ethyleneglycol). Nonvinyl or bimodal secondary crosslinkers have been used. Examples of nonvinyl crosslinkers include glycerol, various molecular weight poly(ethyleneglycols), and ethyleneglycol diglycidyl ether. Bimodal crosslinkers include hydroxyethyl acrylate and acrylate or methacrylate esters of polyethylene glycols. The preferred oxidizing agent is sodium or potassium chlorate. The amount of chlorate affects the reduction in the level of unreacted monomer, the amount of extractable polymer in the product, and the final swelling capacity. Figure 3.10 is a graph of data from examples 78–86 of Burgert et al.,¹¹² in which polymer samples were heated for 20 min after reaching 200°C. As the level of chlorate increases, swelling capacity and extractable polymer increase. The optimum chlorate level, considering swelling capacity, extractable polymer, absorbency under load, and unreacted monomer, is about 200 ppm. The moisture remaining in the particle, after drying and grinding and prior to the reaction step, influences the magnitude of the observed oxidizer effect.

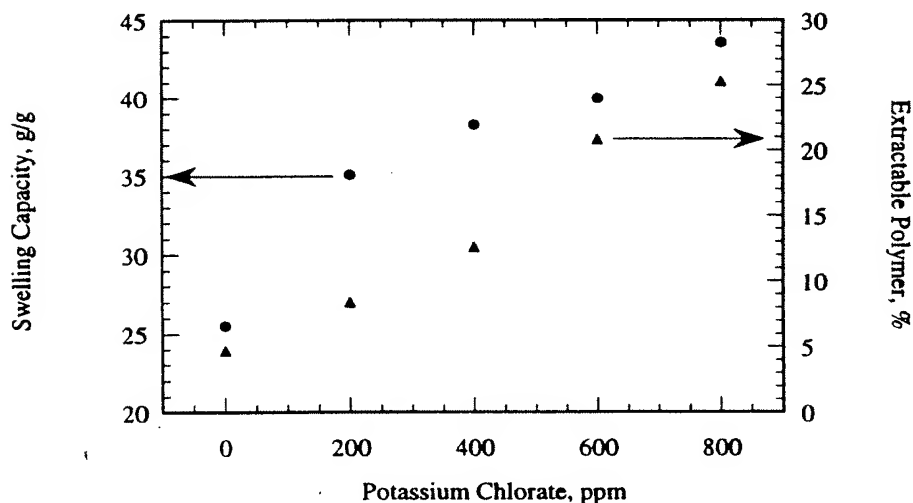


Figure 3.10. The effect of chlorate level on the swelling capacity (●) and extractable polymer (▲) of structured particle product made by the process of Burgert et al.¹¹²

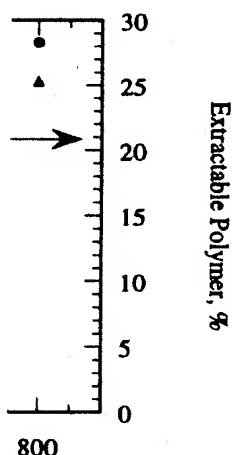
The reaction time should be less when the heating to 10–30 min yielded monomer, and absorbency under load, even at nearly equivalent to sumably because of density.

A consequence of degradation of polymer methods for handling particle surface fracture means of preventing addition of about 10 proves the fracture the superabsorbent polymer" also reduces the particle surface

3.2.8.2. Additives: final product including crosslinking, as described additives.¹¹⁵ Both to (less than 10 μm in other or to larger particles typically blended in active additive to reduce surface crosslinking reaction

Additives that reduce improve polymer flow scope of this problem humid air. In a matter as required in process ate or eliminate this. However, particularly monly available in dry adequate dry flow or rials for use with l copolymers of acryl polyalkylene glycol lamide).¹¹⁸ Quaternary alone or in combination the silica anti-caking types of commercial

structured particle in or combinations of nts have dramatical- this technology, all they are mixed uni- nkers may be used niformly distributed used include 1,1,1- allyl methacrylate, neglycol). Nonvinyl nonvinyl crosslink- glycols), and ethyl- cyethyl acrylate and preferred oxidizing effects the reduction olymer in the prod- data from examples ted for 20 min after icity and extractable elling capacity, ex- omer, is about 200 rinding and prior to izer effect.



and extractable polymer

The reaction temperature should be between 170° and 235°C, and the heating time should be less than 40 min. The best combination of product properties occurs when the heating temperature is between 210°–230°C. Heating times at 230°C of 10–30 min yielded product with nearly the same swelling capacity, extractable polymer, and absorbency under load. Combinations of swelling capacity and absorbency under load, even at high imposed loads, made by this technology (Tables 3.6) are nearly equivalent to properties achieved with surface crosslinking technology, presumably because gel-blocking is limited by a surface layer of higher crosslink density.

A consequence of the “core-shell” particle structure (Fig. 3.9) is a vulnerability to degradation of product quality by fracture of the particle surface.⁸² High-quality methods for handling the solid product are required (see section 3.2.6) to avoid particle surface fracture and consequent degradation of product properties. Chemical means of preventing surface degradation have also been disclosed. For example, the addition of about 10 mol% of a monomer such as poly(ethylene glycol) acrylate improves the fracture resistance of the resulting superabsorbent product.¹¹³ Coating the superabsorbent particles with a “non-reactive, water-insoluble, film-forming polymer” also reduces the dust level (small particle size fraction from abrasion of the particle surface in a ball mill test).¹¹⁴

3.2.8.2. Additives for Improved Handling. Techniques to reduce dust in the final product include agglomeration of the finer dusty particles via surface crosslinking, as described above, or the addition of low levels of hydrophilic liquid additives.¹¹⁵ Both techniques reduce the concentration of air-borne respirable dust (less than 10 μm in diameter) by agglomerating the fine particles either to one another or to larger particles. When low levels of liquid additives are used, they are typically blended into the final product just prior to packaging. In one case, a nonreactive additive to reduce product dustiness may be added concurrently with any surface crosslinking reagents.¹¹⁰

Additives that reduce the rate of moisture absorption in humid environments and improve polymer flow characteristics are also of interest. One can appreciate the scope of this problem by simply exposing a quantity of superabsorbent polymer to humid air. In a matter of a few hours, the polymer begins to clump and will not flow as required in processing in a diaper plant. Dehumidified air may be used to alleviate or eliminate this problem, either in polymer or end-use manufacturing plants. However, particularly in the tropical Pacific markets, dehumidified air is not commonly available in diaper manufacturing plants, and additives must be used to allow adequate dry flow of the polymer. A number of such additives are known: oily materials for use with hygroscopic fertilizers,¹¹⁶ polymeric soaps as drying aids for copolymers of acrylamide,¹¹⁷ and particulate silica in combination with polyols or polyalkylene glycols as a flow aid for polymers and copolymers of poly(acrylamide).¹¹⁸ Quaternary surfactants have also been found useful as anti-clump aids, alone or in combination with additives, to reduce product dustiness (a drawback of the silica anti-caking technology).¹¹⁹ These chemicals may be added in a variety of types of commercial blenders.